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Laser-induced surface acoustic waves: An alternative method to nanoindentation for the mechanical characterization of porous nanostructured thin film electrode media

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ABSTRACT

The mechanical characterization of electrode materials in thin film lithium ion batteries is currently a sparse area. However, mechanical studies could offer valuable insight since the performance and breakdown of active materials is electromechanically coupled. In this paper, a porous nanostructured V_2O_5 cathode thin film with demonstrated high electrochemical performance was investigated by a laser-induced surface acoustic wave technique (LiSAW) that mitigates some of the challenges associated with the popular nanoindentation technique. The intent was to explore the capability of LiSAW in measuring the elastic modulus of the nanostructured film such that a reliable methodology could be produced to mechanically characterize challenging electrode materials. LiSAW measured a modulus of 53 ± 4 GPa for the porous V_2O_5 film and had no problems coping with the 40 nm roughness and delicate structure. On the other hand, nanoindentation produced a modulus of 50 ± 10 GPa, which is comparable to LiSAW, but with considerably higher uncertainty from roughness. For porous nanostructured electrodes, and other challenging films, that are too soft, thin, or delicate for traditional nanoindentation measurements, LiSAW is a potentially excellent alternative. LiSAW testing on many other electrode materials would be instrumental in developing a better understanding between the mechanical and electrochemical properties of thin film battery materials.

1. Introduction

Lithium ion batteries are an integral part of today's energy storage landscape, but the constant miniaturization of electronic devices is currently challenging the technology to fit into reduced form factors. While smaller electronics have allowed for great advancement in many areas such as portable consumer electronics and biologically implantable devices (Holmes, 2001), their energy requirements can often remain similar, if not greater than, before (Whittingham, 2012). Thin film Li-ion batteries are capable of meeting the limited size requirements, but alternatives to the traditional graphite and lithium metal oxide electrode materials are necessary to maintain capacity and performance with diminished battery mass (Ji et al., 2011; Ellis et al., 2010). Nanostructured materials are of interest in this field because they can exhibit very high surface energies which enhance charge transfer kinetics and ion storage capacity (Liu and Cao, 2010; Song et al., 2011; Zhang et al., 2013). Additionally, nanostructures, especially when coupled with porosity, can be more tolerant to the large physical deformations associated with Li-ion insertion and removal thus reducing the mechanical

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breakdown of the electrode and improving the battery life cycle (Vu et al., 2012; Hayner et al., 2012).

It is well known that the effects of the electrode volume change during each charge cycle, producing modest strains of 2% in $LiCoO_2$ cathodes (Reimers and Dahn, 1992) and 7% in $LiFePO_4$ cathodes (Meethong et al., 2007), contributes greatly to the loss of charge capacity over time (Cabana et al., 2010). Yet for such a mechanically rich process, there has been relatively little investigation correlating the breakdown to the mechanical properties of the electrode. While many studies have targeted and identified the main degradation mechanism, the proliferation of micro-cracks (Ebner et al., 2013), comprehensive mechanical design criteria to mitigate such issues in new electrode materials have yet to be determined. With many other electrochemical considerations to contend with, it is easy to see why mechanical aspects are often overlooked, but with links between mechanics and rate capability (Meethong et al., 2007) and the emergence of higher capacity materials with larger expected volume changes, nanomechanical characterization may become critical in understanding optimal electrode design.

The prevalence of nanoindentation in thin film mechanical analysis is especially valuable to the characterization of thin film electrodes. Indentation tests can quickly determine the elastic and plastic properties of a material with the elastic modulus being especially useful here. While electrode degradation is a complex problem with both electrochemical and mechanical considerations, the modulus can breathe insight into the flexibility and reliability of a material and thus aid in understanding how it may cope with lithiation induced strain. Several recent studies have successfully applied nanoindentation to electrode materials. Qu et al. reported on the elastic modulus, density, and fracture toughness of individual $LiCoO_2$ grains and noted that the experimentally determined modulus of 174 GPa was much lower than the previously predicted value of 315–516 GPa (Qu et al., 2012). This suggests a more compliant structure than once thought. Ramdon and Bhushan reported on the elastic modulus, hardness, and wear properties of $LiFePO_4$ cathodes before and after multiple charge cycles (Ramdon and Bhushan, 2014). They found that the modulus did not change significantly through cycling, but that the hardness increased by almost 100% giving rise to a durable, yet brittle structure. Zhu et al. performed indentations on RuO_2 anodes and found that the elastic modulus decreases by an order of magnitude after 50 cycles (Zhu et al., 2013). With such a limited quantity of studies, it is difficult to correlate the elastic modulus, or any other mechanical property, to battery performance over time therefore this area demands further investigation.

The lack of nanomechanical studies could possibly be attributed to the difficulty of nanoindentation on thin film electrode materials. For consistent results that are free of indentation substrate effects, it is necessary to have films with low surface roughness and a thickness many times that of the penetration depth. This can be especially problematic to nanostructured or porous films since their engineered roughness may be too delicate for mechanical polishing and their thicknesses could be very small. While substrate effects from low thicknesses can be overcome by utilizing an alternative indentation analysis scheme (Li and Vlassak, 2009), albeit with significant computational intensity, defeating roughness through deep indents may not always be viable. In this scenario, it may be more efficient to use a laser-induced surface acoustic wave (LiSAW) technique to determine the elastic modulus.

The LiSAW technique is valuable to thin and porous films because it requires only elastic deformations, it features non-contact measurements, and the mechanical property extraction naturally considers and isolates substrate coupling (Hess, 1996; Schneider and Tucker, 1996; Xiao et al., 2011). In the experiment, an Nd:YAG laser is used to excite Rayleigh waves that subsequently propagate across the layered system. Due to elastic mismatch between the film and substrate, frequency dispersion of the wave occurs. Since the relationship between mechanical properties and dispersion is well documented in wave mechanics (Farnell and Adler, 1972), LiSAW can seek unknown parameters of the film or substrate by experimentally quantifying the dispersion. In this manner, if enough nonlinearity exists in the dispersion curve, the film thicknesses, Poisson's ratios, densities, and elastic moduli of the materials involved can be found. Typically, many of these parameters are known at the onset, thus only one or two parameters may require fitting. LiSAW can deliver these results on the same time-scale as typical indentation tests and with no substrate influence. Due to the micron scale of SAW wavelengths, the technique can work well on moderately rough films (Cote et al., 2009) and, depending on SAW detection scheme, with little or no surface preparation. While the LiSAW technique requires an area millimeters in scale for adequate wave dispersion with existing detection schemes, the creation of uniform blanket films of electronic materials is typically not a major challenge. Rather, it is the thickness of such films that creates the greatest characterization challenge and LiSAW directly addresses and excels at these geometries based on the inherently coupled film-substrate analysis procedure.

The limiting factor of many current Li-ion batteries lies in the low energy density of the cathode. Common cathode materials based on layered lithium metal oxides such as $LiCoO_2$ and $LiFePO_4$ have capacities of just 140 mA h g^{-1} and 170 mA h g^{-1} respectively (Nazri and Pistoia, 2009). Significant research has been completed on the oxides of other first row transition metals in order to achieve higher capacities. From these studies, vanadium oxides have emerged with great potential due to their wide range of available oxidation states, high reversibility, and favorable layered structures, all of which are conducive to the electrochemical lithiation process (Ding et al., 2009). Specifically, V_2O_5, with a theoretical capacity of 450 mA h g^{-1} (Liu et al., 2011a), has been extensively studied and remains a leading candidate amongst alternative cathode materials. While V_2O_5 has been known for inadequate structural stability and slow electrochemical kinetics, nanostructured V_2O_5 forms have recently been shown to overcome these challenges by demonstrating excellent capacity, rate capability, and cyclability (Liu et al., 2011b; Pomerantseva et al., 2012; Augustyn and Dunn, 2010).